

MARKED SPECIFICATION

F-6998

Ser. No. 09/864,778



RUBBER COMPOSITION FOR ADHERING TO STEEL CORDS

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a rubber composition for adhering to steel  
5 cords and particularly to a rubber composition for adhering to steel cords which is  
excellent in adhesion to steel cords.

DESCRIPTION OF THE RELATED ART

In order to increase the adhesive force of rubber to steel cords plated with  
brass, bronze, or zinc, a cobalt salt of an organic acid has heretofore been exclusively  
10 been used so far. That is, there exists a A technique where involving blending of the  
cobalt salt of an organic acid with a rubber composition promotes to promote the  
formation of an adhesive interface layer onto steel cords, thus to increase increasing  
the adhesive force, is known in the art.

In recent years, problems have been generated occurred, such as deterioration  
15 in adhesive force caused by high exothermic heat accompanied by speeding up or  
power up higher operating speeds and greater horsepower of vehicles, deterioration  
in adhesive force caused by thermal history heat, accompanied by prolonged lifetime  
of tires tire life, or deterioration in adhesive force caused by moisture and heat over  
a period of time which elapses between manufacture and travel (a storing time from

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manufacture to use, containing a time of practical use), and thus requiring adhesive properties of a higher level ~~have been demanded~~.

Although ~~the~~ cobalt is excellent in initial adhesion, heat deterioration (heat aging) causes serious deterioration in adhesive force as described above. ~~The~~ Even  
5 the use of cobalt ~~cannot be satisfying any more~~ can no longer alone satisfy the needs  
for the high level of adhesion performance ~~of a high level~~ required in recent years.

It is probable that ~~the~~ cobalt ~~has~~ is a strong ~~action to promote~~ oxidation promoter, and the action thereof to promote the formation of an adhesive layer causes an increase in the thickness of the adhesive layer ~~in-terminal~~ during travel to lead to  
10 fracture of the rubber layer.

~~The cobalt~~ Moreover, cobalt is a rare metal, and countries producing the raw material ~~thereof may be politically unstable~~ have had problems with political stability. Accordingly, the use of cobalt is disadvantageous ~~in~~ because of high fluctuation in price and an unstable supply of rubber products.

## SUMMARY OF THE INVENTION

The invention has been ~~carried out~~ made under the aforesaid circumstances. An ~~aim~~ object of the invention is to provide a rubber composition for adhering to steel cords, ~~composition~~ which has excellent heat-resistant adhesion and moist heat-resistant adhesion, as well as excellent initial adhesion and performance ~~of~~ at a level

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~~similar~~ comparable to or higher than that in the related art, as to resistance to rubber fracture.

~~A The rubber composition for adhering to steel cords as described in claim 1 is a rubber composition~~ according to embodiments of the present invention  
5 demonstrates excellent ~~in~~ adhesion to steel cords. The rubber composition is prepared by adding the following components (A) and (B) to 100 weight parts of a rubber component containing natural rubber and/or a diene synthetic rubber.

(A) A mixture of a compound containing nickel, and a compound containing molybdenum; or a compound containing simultaneously nickel, and molybdenum in  
10 a metal-converted amount of 0.01 to 10 weight parts.

(B) (b1) 0.2 to 20 weight parts of hexamethylenetetramine or a melamine derivative, and (b2) 0.1 to 10 weight parts of at least one selected from the group consisting of phenol resins, resorcin, resorcin derivatives, and cresol resins.

A composition ~~as described in claim 2~~ according to certain embodiments of  
15 the present invention is prepared by further adding a compound containing calcium (C) ~~in to the foregoing composition as described in claim 1.~~

~~A The composition as described in claim 3~~ according to those embodiments  
of the present invention is prepared by adding the aforesaid compound containing calcium (C) in an amount of 0.1 to 20% in weight ratio to the aforesaid component  
20 (A) ~~in~~ of the basic composition as described in claim 2.

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~~A composition as described in claim 4 is~~ Compositions according to still  
other embodiments of the present invention are prepared by further adding silica (D)  
~~in to the basic composition as described in any one of claims 1 to 3~~ or to the calcium-  
containing composition.

5       ~~A composition as described in claim 5 is~~ These silica-containing compounds  
are prepared by adding 1 to 100 weight parts of the aforesaid silica (D) to 100 weight  
parts of the rubber component in the composition as described in claim 4 of the basic  
or calcium-containing compositions.

10       The invention ~~can provide~~ provides a rubber composition for adhering to steel  
cords which has excellent heat-resistant adhesion and excellent moist heat-resistant  
adhesion, as well as excellent initial adhesion and performance ~~of at~~ at a level ~~similar~~  
comparable to or higher than that in the related art, as to resistance to rubber fracture.

## DETAILED DESCRIPTION OF THE INVENTION

### Rubber Components

15       Examples of rubber components used in the invention include natural rubber  
and synthetic rubber such as polyisoprene rubber (IR), polybutadiene rubber (BR),  
styrene-butadiene rubber (SBR), isoprene-isobutylene rubber (IIR), ethylene-  
propylene-diene rubber (EPDM), and modified rubber thereof. These can be used  
singly or as a mixture of two or more thereof.

Component (A)

The compound containing nickel, and the compound containing molybdenum ~~can be~~ are both either an inorganic compound or an organic compound, respectively.

~~The inorganic~~ Inorganic compounds include nickel oxide, and molybdenum  
5 oxide; nickel sulfate, and molybdenum sulfate; nickel phosphate, and molybdenum  
phosphate; nickel phosphite, and molybdenum phosphite; nickel carbonate, and  
molybdenum carbonate; and nickel chloride, and molybdenum chloride.

~~The organic~~ Organic compounds include nickel salts, and molybdenum salts  
of organic acids; and an organonickel sulfur compound, an organomolybdenum  
10 sulfur compound.

~~Herein, preferred~~ Preferred nickel salts of organic acids are nickel  
naphthenate, nickel octylate, nickel propionate, nickel abietate, and nickel acetate in  
view of excellent adhesion performance.

Preferred molybdenum salts of organic acids are molybdenum naphthenate  
15 and/or molybdenum abietate in view of excellent adhesion performance.

In component (A), a Ni/Mo ratio (weight converted to metals) is not  
particularly limited, but preferably is from 2/1 to 20/1. The ratio less than 2/1 may  
invite problems of being uneconomical (Mo is very costly as compared with Ni) and  
decreasing hardness (rigidity) of the resulting rubber. Exceeding 20/1 may ~~invite~~

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cause a problem of being unable to acquire sufficient adhesion (Ni cannot compensate for deterioration in adhesion).

In these salts of organic acids, it also is possible to blend organic acids. For example, adhesion, particularly moist heat adhesion is preferably improved when  
5 component (A) is a mixture of nickel salts of naphthenic acid and octylic acid (naphthenic acid/octylic acid = 1/1 to 1/4 in weight percent) and a molybdenum salt of naphthenic acid.

Naphthenic acid is preferred ~~on the grounds that~~ because the high acid value  
cf, for example, 250 mgKOH/g or more, further improves the adhesion, particularly  
10 the heat-resistant adhesion.

Component (B)

A Component (B) includes combination of the following components (b1)  
and (b2) ~~composes component (B) of the invention.~~

(b1) hexamethylenetetramine or melamine derivatives.

15 (b2) at least one selected from the group consisting of phenol resins, resorcin, resorcin derivatives, and cresol resins.

An example of the melamine derivatives is hexamethoxymethylmelamine.

Examples of the resorcin derivatives include resorcin/ alkylphenol/formalin copolymers and resorcin/formalin reaction products.

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Component (B) is used to markedly improve ~~markedly~~ the adhesion, particularly the initial adhesion.

### Component (C)

Use of compounds containing calcium (C) is preferred ~~on the grounds~~  
5 because of further improving the adhesion, particularly ~~the~~ heat-resistant adhesion.

Examples of compounds containing calcium (C) include calcium borate and calcium neodecanoate, but are not limited to these salts.

Compounds containing calcium (C) are preferably added to component (A) during the preparation thereof on the grounds that an effect of improving the  
10 hardness (rigidity) of the resulting rubber can be acquired (When component (C) is added to rubber singly apart from component (A), such effect ~~can~~ is not be obtained).

### Component (D)

Addition of silica (component (D)) ~~can~~ further ~~improve~~ improves the adhesion. Silica used include dry process silica (silicic acid anhydride) and wet  
15 process silica (hydrated silicic acid), but are not ~~particularly~~ thus limited.

### Carbon Black

Carbon black usable in the invention is ~~not particularly limited~~ generally

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unlimited, and include carbon blacks classified according to the classification by ASTM D1765, ~~include~~ including SAF class having numbers of 100's, ISAF class having numbers of 200's, and HAF class having numbers of 300's which have a high reinforcing action, and ~~concretely~~ particularly include N110, N121, N219, N220, N231, N330, and N339. These can be used singly or as a mixture of two or more thereof.

### [[The Rest (Ratio)] Blend Ratios of [[Blend]] Principal and [[Others]] Other Components

The ratio of component (A) blended is from 0.01 to 10 weight parts (in conversion to metal) to 100 weight parts of the rubber component. The ratio of component (A) less than 0.01 weight part invites a problem of failing to obtain sufficient initial adhesion. Exceeding 10 weight parts results in promoting oxidative deterioration of rubber by metal and decreasing aging resistance of the rubber, and as a result offers a problem of decreasing adhesion after aging. The range is preferably from 0.01 to 5.0 weight parts, and more preferably from 0.01 to 2.0 weight parts (in conversion to metal).

~~About~~ In component (B), the ratio of component (b1) blended is from 0.2 to 20 weight parts to 100 weight parts of the rubber component. The ratio of



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component (b2) blended is from 0.1 to 10 weight parts to 100 weight parts of the rubber component (The ratio varies depending upon purposes and kinds of resins used and cannot be unconditionally determined). When the ratio of component (b1) blended is less than 0.2 weight part or the ratio of component (b2) is less than 0.1 weight part to 100 weight parts of the rubber component, an effect of improving the adhesion cannot be sufficiently achieved. The ratio of component (b1) blended exceeding 20 weight parts or the ratio of component (b2) exceeding 10 weight parts makes the rubber resinous and fragile. Herein, a preferred range of component (b1) is from 0.5 to 10 weight parts, and that of component (b2) is from 0.5 to 5.0 weight parts.

The ratio of a compound containing calcium (C) blended is from 0.1 to 20 percent in weight ratio to component (A). The ratio of component (c) blended is less than 0.1 weight percent fails to achieve sufficient improvement in heat-resistant adhesion whereas exceeding 20 weight percent makes it difficult to prepare component (A). Herein, a preferred range is from 1 to 10 weight percent.

The ratio of sulfur blended is not particularly limited, and for example, from 1 to 10 weight percent.

## EXAMPLES

The invention is illustrated through examples, but is not to be construed as

limited by the examples.

### Examples and Comparative Examples

Common components as described in the following “table 1” and respective components as described in the following “tables 2 to [[5]] 4” were blended in ratios as described in the tables. Thereafter, these components were kneaded by use of a Banbury mixer according to a general procedure to prepare rubber compositions. About the resulting rubber compositions, an adhesion test (initial adhesion, heat-resistant adhesion, moist heat-resistant adhesion) and an aging resistance test were carried out and evaluated. The respective procedures of evaluation are as follows:

#### (1) Adhesion Test

Steel cords plated with brass were arranged at intervals of 12 lengths/25 mm and separated by seating rubber to be evaluated. Two sheets of such rubber were piled and vulcanized at 150°C for 30 min to prepare a sample. Peel force of the sample of 25-mm width was measured by use of an autograph. A covering ratio by the steel cord rubber was evaluated by inspection with the naked eye.

The initial adhesion, heat-resistant adhesion, and moist heat-resistant adhesion were evaluated (Heat-resistant adhesion: undergoing aging in a 160°C oven to evaluate adhesion. Moist heat-resistant adhesion: A sample is placed in an autoclave containing water and subjected to aging in a 105°C oven to evaluate adhesion). Results of measurements were estimated by indexes based on the results

of Comparative Example 1 estimated as 100 and described in Tables 2 to [[5]] 4.

(2) Aging Resistance Test

After aging in a Geer oven (after aging a sample in the 90°C oven), a tensile test was carried out (according to JIS K6253). Retention degrees of breaking extension to the initial value were represented by indexes based on the result of Comparative Example 1 estimated as 100. Resulted are described in Tables 2 to [[5]] 4.

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Table 1

Natural Rubber	100 parts
Carbon Black (HAF)	60 parts
Zinc White	8 parts
Aging Preventive (6C)	2 parts
Insoluble Sulfur	6 parts
Promoter (DZ)	1 part

Table 2

	Comparative Example				
	1	2	3	4	5
Cobalt Stearate	○				
Ni / Mo Sample 1 * <sup>1</sup>					
Ni / Mo Sample 2 * <sup>2</sup>					
Ni / Mo Sample 3 * <sup>3</sup>		○		○	○
Ni / Mo Sample 4 * <sup>4</sup>					
Ni / Mo Sample 5 * <sup>5</sup>					
Ni / Mo Sample 6 * <sup>6</sup>					
Ni / Mo Sample 7 * <sup>7</sup>					
Ni / Mo Sample 8 * <sup>8</sup>					
Amount of the aforesaid Metallic Compound Blended to 100 Parts of Rubber Component (Amount Converted to Metal) (Part)	0.2	0.2		0.005	15
SUMIKANOL 620 (Sumitomo Chemical Co., Ltd.) * <sup>9</sup>	2		2	2	2
SCILETTU 963L (Mitsui Scitech) * <sup>10</sup>	4		4	4	4
Initial Adhesion					
Peel Force	100	82	76	73	101
Covering Ratio of Rubber	100	100	100	100	100
Heat-Resistant Adhesion (160°C×96h age)					
Peel Force	100	75	88	110	82
Covering Ratio of Rubber	50	50	60	90	60
Moist Heat Adhesion (105°C×96h steam age)					
Peel Force	100	83	105	106	88
Covering Ratio of Rubber	10	10	10	10	5
Aging Resistance (90°C×192h age)					
Degree of Improvement	100	106	110	127	85

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Table 3

	Example					
	1	2	3	4	5	6
<b>Cobalt Stearate</b>						
<b>Ni / Mo Sample 1</b> * <sup>1</sup>	○					
<b>Ni / Mo Sample 2</b> * <sup>2</sup>		○				
<b>Ni / Mo Sample 3</b> * <sup>3</sup>			○			
<b>Ni / Mo Sample 4</b> * <sup>4</sup>				○		
<b>Ni / Mo Sample 5</b> * <sup>5</sup>					○	
<b>Ni / Mo Sample 6</b> * <sup>6</sup>						○
<b>Ni / Mo Sample 7</b> * <sup>7</sup>						
<b>Ni / Mo Sample 8</b> * <sup>8</sup>						
<b>Amount of the aforesaid Metallic Compound Blended to 100 Parts of Rubber Component (Amount Converted to Metal) (Part)</b>	0.2	0.2	0.2	0.2	0.2	0.2
<b>SUMIKANOL 620 (Sumitomo Chemical Co., Ltd.)</b> * <sup>9</sup>	2	2	2	2	2	2
<b>SCILETTU 963L (Mitsui Scitech)</b> * <sup>10</sup>	4	4	4	4	4	4
<b>Initial Adhesion</b>						
Peel Force	111	114	116	115	111	117
Covering Ratio of Rubber	100	100	100	100	100	100
<b>Heat-Resistant Adhesion (160°C×96h age)</b>						
Peel Force	93	98	100	99	100	96
Covering Ratio of Rubber	80	80	90	80	70	90
<b>Moist Heat-resistant Adhesion (105°C×96h steam age)</b>						
Peel Force	106	104	105	104	106	99
Covering Ratio of Rubber	20	15	10	10	10	20
<b>Aging Resistance (90°C×192h age)</b>						
Degree of Improvement	113	112	111	112	111	100

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Table 4

	Example						
	7	8	9	10	11	12	13
<b>Cobalt Stearate</b>							
<b>Ni / Mo Sample 1</b> * <sup>1</sup>							
<b>Ni / Mo Sample 2</b> * <sup>2</sup>							
<b>Ni / Mo Sample 3</b> * <sup>3</sup>			○	○	○	○	○
<b>Ni / Mo Sample 4</b> * <sup>4</sup>							
<b>Ni / Mo Sample 5</b> * <sup>5</sup>							
<b>Ni / Mo Sample 6</b> * <sup>6</sup>							
<b>Ni / Mo Sample 7</b> * <sup>7</sup>	○						
<b>Ni / Mo Sample 8</b> * <sup>8</sup>		○					
<b>Amount of the aforesaid Metallic Compound Blended to 100 Parts of Rubber Component (Amount Converted to Metal) (Part)</b>	0.2	0.2	0.2	0.2	0.2	0.2	0.2
<b>SUMIKANOL 620 (Sumitomo Chemical Co., Ltd.)</b> * <sup>9</sup>	2	2	8			2	2
<b>Resorcin/Formalin Reaction Product PENACOLITE RESIN B19-S (Indospech Co.)</b>				2			
<b>Resorcin (Sumitomo Chemical Co., Ltd.)</b>					2		
<b>SCILETTU 963L (Mitsui Scitech)</b> * <sup>12</sup>	4	4	10	4	4		4
<b>Hexamethylenetetramine NOXELER H (Ouchi Shinko Kagaku K. K.)</b>						4	
<b>Silica (NIPSEAL AQ, Nippon Silica K. K.)</b>							10
<b>Initial Adhesion</b>							
Peel Force	105	114	116	114	118	114	105
Covering Ratio of Rubber	100	100	100	100	100	100	100
<b>Heat-Resistant Adhesion (160°C×96h age)</b>							
Peel Force	99	104	114	102	98	98	97
Covering Ratio of Rubber	80	70	90	90	90	90	90
<b>Moist Heat-Resistant Adhesion (105°C×96h steam age)</b>							
Peel Force	91	95	127	103	107	103	100
Covering Ratio of Rubber	30	10	30	10	10	15	40
<b>Aging Resistance (90°C×192h age)</b>							
Degree of Improvement	113	107	111	113	109	111	110

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- \*1) Ni naphthenate/Mo naphthenate (Ni/Mo = 2/1 (mole ratio))
- \*2) Ni naphthenate/Mo naphthenate (Ni/Mo = 4/1 (mole ratio))
- \*3) Ni naphthenate/Mo naphthenate (Ni/Mo = 6/1 (mole ratio))
- \*4) Ni naphthenate/Mo naphthenate (Ni/Mo = 8/1 (mole ratio))
- 5 \*5) Ni naphthenate/Mo naphthenate (Ni/Mo = 20/1 (mole ratio))
- \*6) Ni naphthenate/Mo naphthenate of high acid value (300 mgKOH/g) (Ni/Mo = 6/1 (mole ratio))
- \*7) (Ni octylate + Ni naphthenate [octylic acid : naphthenic acid = 7 : 3])/Mo naphthenate (Ni/Mo = 6/1 (mole ratio))
- 10 \*8) Ni naphthenate/Mo naphthenate (Ni/Mo = 6/1 (mole ratio)) and Ca borate at a weight ratio of 2%
- \*9) Resorcin/alkylphenol/formalin copolymer resin
- \*10) Hexamethoxymethylmelamine

ABSTRACT

The invention aims at providing a A rubber composition for adhering to steel cords ~~which is~~ having excellent in heat-resistant adhesion and moist heat-resistant adhesion, as well as initial adhesion, and ~~has performance of~~ at a level ~~similar~~ comparable to or higher than that of the related art in resistance to rubber fracture, ~~wherein the following is made from~~ components (A) and (B), which are blended to 100 weight parts of rubber components containing natural rubber and/or diene synthetic rubber~~[[:]]~~ wherein ~~Component~~ component (A) ~~[[:]]~~ is a mixture of a compound containing nickel and a compound containing molybdenum; or a compound containing nickel and molybdenum simultaneously, in a metal-converted amount of 0.01 to 10 weight parts~~[[.]]~~ ; and ~~Component~~ component (B) ~~[[:]]~~ is a mixture of (b1) which is 0.2 to 20 weight parts of hexamethylenetetramine or a melamine derivative, and (b2) which is 0.1 to 10 weight parts of at least one selected from the group consisting of phenol resins, resorcin, resorcin derivatives, and cresol resins.